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Synthesis of silver nanoparticles embedded on silica by gamma irradiation for utilization as antimicrobial agents

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Abstract: Silver nanoparticles deposited on silica (Ag nano/SiO_2) have been prepared by Co-60 gamma irradiation of a mixture containing Ag^+, SiO_2, H_2O and ethanol. The reduction of Ag^+ within the SiO_2 suspension was facilitated by e^-_{aq} and $H^\bullet$ generated during the radiolysis of solvent (water/ethanol). The presence of SiO_2 effectively prevented the clustering of Ag particles. The conversion dose ($Ag^+ \rightarrow Ag^0$) was investigated with UV-Vis spectroscopy. The results revealed that Ag nanoparticles with the sizes of 5-20 nm were formed from the mixture of 5 mM Ag^+ as observed by Transmission electron microscopy (TEM). The crystal structure of Ag nanoparticles was further analyzed by using X-ray diffraction (XRD). In addition, the antifungal activity of Ag nano/SiO_2 was also assessed against *Aspergillus niger* van Tieghem using plate count method. The results indicated that the antifungal efficacy of Ag nano/SiO_2 reached approximately 64%, 71%, 81%, 82%, and 96% at Ag nanoparticle concentrations of 30 ppm, 50 ppm, 70 ppm, 100 ppm, and 150 ppm, respectively.

Keywords: *silver nanoparticles, silica, gamma irradiation, antimicrobial agent.*

I. INTRODUCTION

The preparation of metal nanoparticles is interesting in the current studies because of the electronic, magnetic and optical properties which are different from both the ion and bulk materials [1, 2]. Among them, silver (Ag) nanoparticles are known to have antibacterial, antifungal activity and relatively high safety [3, 4]. Many various methods have been used for the synthesis of Ag nanoparticles such as chemical reduction, photoreduction, microwave-assisted polyol, gamma irradiation, [5-9]. Gamma irradiation has been considered a useful method for the preparation of silver nanoparticles [4]. Solvated electron (e^-_{aq}), hydrogen atom ($^\bullet H$) formed during gamma-radiolysis of aqueous solution reduce silver ion (Ag^+) to silver atom (Ag^0) [10].

Various studies have explored the use of inorganic materials such as silica (SiO_2), zeolite, titanium oxide (TiO_2), aluminum oxide (Al_2O_3) as carriers to produce Ag nanoparticles [3, 5, 6, 11, 12]. Among these materials, SiO_2 is widely used to encapsulate Ag nanoparticles because it has high thermal stability, chemical resistance, creating transparent suspension and preventing caking [6, 11-14]. In a prior phase of our research, the Ag nanoparticles have been synthesized by Co-60 gamma irradiation with alginate as a stabilizing agent [15]. The purpose of this study is prepare the Ag nanoparticles embedded on SiO_2 by Co-60 gamma irradiation and characterize them for further application. Antifungal activity of the resulting Ag nano/SiO_2 was also investigated against *Aspergillus niger* van Tieghem.

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II. THE MAIN PART OF THE REPORT

A. Research subjects and methodology

Silver nitrate ($AgNO_3$) and ethanol used in the present study were purchased from Shanghai Chemical Reagent Co., China at analytical grade. Silica (SiO_2) with average particle sizes from 0.2 to 0.3 nm was supplied by Cabot Corp. (USA). Distilled water was used in all experiments. Sabouraud agar was used as a selective medium for fungal culture, was purchased from India. A strain of fungus was isolated from the house wall employing the direct sampling method with identified name *Aspergillus niger* van Tieghem.

Firstly, SiO_2 powder was added into ethanol, soaked for 1 hour and stirred to prepare SiO_2 suspension. Second, $AgNO_3$ was dissolved in water and Ag^+ solution was slowly poured into the SiO_2 suspension during stirring to form the sample containing 9% (w/v) SiO_2, and 5 mM Ag^+ in admixture solvent of 80% (v/v) ethanol and 20% H_2O, then continuously stirred for further 20 minutes. The mixture of Ag^+/SiO_2 was put into glass bottles with seals before gamma irradiation. The irradiation was carried out under the Co-60 irradiator (SVST Co-60/B, Hungary), the irradiation doses ranges from 4 to 20 kGy and dose rate of ~1.25 kGy/h at VINAGAMMA Center (HCM City).

UV-Vis spectrometry: Ag nano/SiO_2 was diluted in distilled water into 0.1 mM solution calculated as Ag^+ concentration, and the absorbance of the solution was recorded using a UV-Vis spectrophotometer (UV-2401PC, Shimadzu, Japan). The saturated dose (D_{bh}) ($Ag^+ \rightarrow Ag^0$) was determined by optical density (OD) at the maximum absorption wavelength (λ_{max}).

TEM photography: size of the Ag nanoparticles entrapped on SiO_2 was determined by using the TEM images on transmission electron microscope (TEM) model JEM-1400, JEOL, Japan. Photoshop CS2 software is used to measure grain size on TEM images.

XRD spectrometry: X-ray diffraction patterns of Ag nano/SiO_2 samples were recorded with a diffractometer (X'Pert PRO, Panalytical, Netherlands) using a CuKα radiation. All samples were scanned in the 2θ range of 10-80^0. Average crystal size (t) of the Ag nanoparticles was calculated from the XRD patterns using the Debye-Scherrer equation as follows [5]:

$$t\ (A^o) = 0.9 \times \lambda / (\beta \times \cos\theta) \qquad (1)$$

Where λ is wavelength of the CuKα radiation (λ = 1.54 A^o), θ is the Bragg angle and β is the width of the peak at the half height (maximum) in radians.

The antimicrobial activity of Ag nano/SiO_2 was tested against *Aspergillus niger* van Tieghem by plate count method. The fungal colonies (~ 10^6 CFU/ml) were incubated in Sabouraud media (Himedia, India) supplemented with Ag nano/SiO_2 powder according to Ag nano concentration of 30, 50, 70, 100 and 150 ppm for 48 h at 30°C. After that, number of viable fungal cells was determined by the TCVN-5165-90 standard [11]. The inhibitory percentage of Ag nano on fungal growth (η) was calculated using the equation:

$$\eta\ (\%) = 100 \times (N_1 - N_2) / N_1 \qquad (2)$$

where N_1 and N_2 are the numbers of viable fungal cells (CFU/ml) in the mediums supplemented without (control) and with Ag nano/SiO_2 at various Ag nano amounts.

B. Results and Discussion

1. Preparation of Ag nano/SiO_2

The UV-Vis spectra of Ag nano/SiO_2 samples formed at different irradiation doses were shown in Fig. 1. As it can be seen in the Figure, the absorption spectra of the irradiated Ag nano/SiO_2 suspensions at the irradiation dose of ~ 4 kGy showed a band at 408 nm corresponding to typical characteristic band of Ag nanoparticles, but this characteristic peak could not be observed in the spectrum of non-irradiated suspension of Ag^+/SiO_2. Wavelength at the maximum absorption (λ_{max}) and absorption intensity at the maximum wavelength of the irradiated suspensions increased with irradiation dose. The λ_{max} of the Ag nano/SiO_2 formed by irradiation at the doses ranging from 4 to 20 kGy were 408-426 nm, respectively. In theory, Ag nanoparticles showed the characteristic absorption bands in the visible region (λ_{max} 390-450 nm) corresponding to their typical surface plasmon resonance peak [9, 12]. Thus, Ag nanoparticles were formed and entrapped onto silica powder by gamma irradiation.

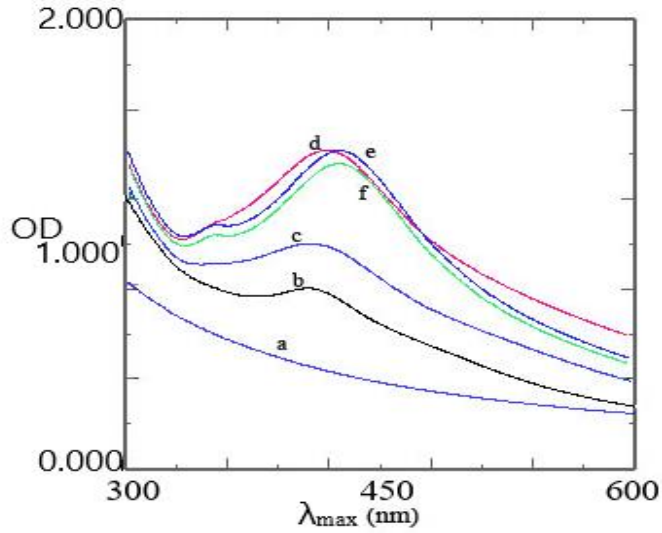

Fig. 1. UV-Vis spectra of Ag nano/SiO_2 samples obtained from 5mM Ag^+ suspensions by gamma irradiation at 0 kGy (a), 4 kGy (b), 8 kGy (c), 12 kGy (d), 16 kGy (e), and 20 kGy (f)

Saturation dose is the irradiation dose required to change completely Ag^+ into Ag^0 [12, 16]. As the irradiation dose increased, the intensity of UV absorption of silver nanoparticles at the maximum wavelength increased, reaching a stable value with the nanoparticles formed by irradiation at 12 kGy. This showed that the irradiation dose of 12 kGy is necessary to convert 5 mM of Ag^+ into Ag^0. In the Ag^+/SiO_2 suspension, an equilibrium between the silver absorbed on the SiO_2 surface and the silver released into the solution may be established [13]. When the suspension containing 5 mM Ag^+ and SiO_2 in 80% ethanol/20% water solvent was irradiated with gamma radiation, the radiolysis of water produced solvated electron (e^-_{aq}), hydrogen atom ($H^\bullet$) and hydroxyl radical ($^\bullet OH$). In which, both e^-_{aq} and $H^\bullet$ are considered strong reducing agents due to their redox potential: E^o (H_2O/e^-_{aq}) = -2.87 V_{NHE} and E^o (H^+/H) = -2.3 V_{NHE} in comparison to E^o (Ag^+/Ag^0) = -1.8 V_{NHE} [14, 15]. These differences in redox potential allows them to effectively reduce the Ag^+ entrapped onto SiO_2 to form zerovalent Ag (Ag^0). However, silver atoms formed on the silica are

susceptible to oxidation back into Ag^+ by $^\bullet OH$ radicals. To prevent this oxidation process, alcohols such as ethanol or isopropanol are used to react with $^\bullet OH$ radicals. This reaction results in the formation of the $CH_3{}^\bullet CHOH$, which in turn acts as reducing agent for the silver ion clusters (Ag^+_n/SiO_2) to convert them into silver atom clusters (Ag^0_n/SiO_2). A more detailed explanation of this process can be found in the literature [16].

In theory, the yield of reducing radicals (e^-_{aq}, $H^\bullet$, $CH_3{}^\bullet CHOH$) was 6 per 100eV of energy deposition during gamma irradiation [12]. To keep it simple, a irradiation dose of 1 kGy could effectively reduce 0.57 mM of Ag^+ [17]. Ramnani et al. [12] reported that a radiation dose of ~0.9 kGy was sufficient to completely convert 0.5 mM of Ag^+ into Ag^0. On the other hand, Sarkany et al. indicated that a higher radiation dose of 8 kGy was required to completely reduce 2.5 mM of Ag^+ in their work [18]. The results of this study suggested that a radiation dose of 1 kGy is necessary to reduce 0.42 mM of Ag^+ into Ag^0, which is lower than what theoretical calculations would predict. This variation may be attributed to the presence of free oxygen in the sample, which could have reduced the efficiency of the reduction process.

Fig. 2 shows TEM image of Ag nano/SiO_2 formed by irradiation of the solution containing 5 mM Ag^+. The size of resulting Ag nanoparticles was ranging from 5 to 20 nm.

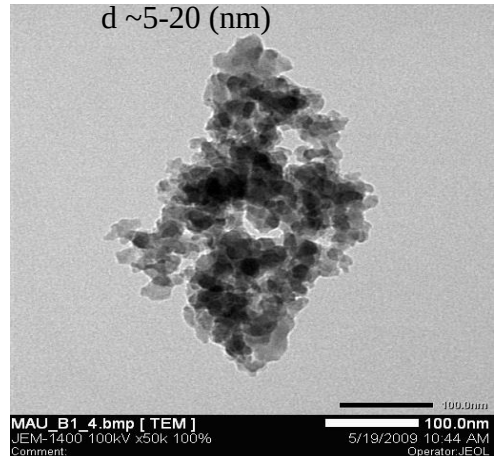

Fig. 2. TEM image of Ag nano/SiO_2 formed from the suspension containing 5 mM Ag^+

The crystal structure of the obtained resulting Ag nano/SiO_2 particles was examined by using a X-ray diffractometer. XRD pattern of SiO_2 (Fig. 3a) displayed a peak at $2\theta = 21.9°$, which indicates indicating that the SiO_2 particles possess amorphous structure [3, 5]. Conversely, when the XRD of Ag nano/SiO_2 outside the characteristic peak of SiO_2 (Fig. 3b) was considered, we observe 4 distinct and prominent characteristic peaks of metallic silver at 2θ of 37.96^o, 44.23^o, 64.22° and 77.23°. These peaks correspond to the 111, 200, 220 and 311 Brags reflections, which clearly demonstrates the FCC (face centered cubic) structure of silver nanoparticles [18]. The average crystal size of silver nanoparticles supported on SiO_2 was determined to be 23 nm based on the XRD spectrum [5]. This result is consistent with the findings reported in the literatures [19, 20].

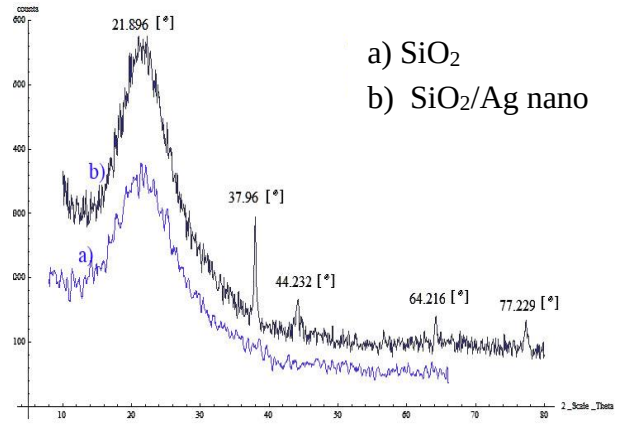

Fig. 3. XRD spectra of SiO_2 (a), Ag nano/SiO_2 (b)

2. Examination of antifungal activity of Ag nano/SiO_2 against Aspergillus niger van Tieghem

Table I shows inhibitory efficiency of Ag nano/SiO_2 contained various amount of Ag nano against *Aspergillus niger* van Tieghem. The antifungal efficiency of Ag nano/SiO_2 material ranged from 64% to 96%, with increasing concentrations of Ag nanoparticles. Specifically, at concentration of 30 ppm, 50 ppm, 70 ppm, 100 ppm, and 150 ppm, the inhibitory efficiencies were 64%, 71%, 81%, 82%, and 96%, respectively (Fig. 4). The higher the concentration of Ag nanoparticles in the Ag nano/SiO_2 was, the stronger the inhibitory efficiency was. At a concentration of 150 ppm, Ag nanoparticles were able to eliminate the number of *Aspergillus* in the liquid medium from 1.8×10^6 to 7.1×10^4 CFU/ml (about 2 log level). The inhibitory efficiency of Ag nano/SiO_2 material depends on various factors, including the size, shape, and concentration of Ag nanoparticles, as well as the nature, developing stage of the fungal cells and the duration of contact between the Ag nanoparticles and microorganisms [2, 3]. Furthermore, the results from the study conducted by Oh et al. also indicated that the antifungal efficiency of Ag nanoparticles against *Botrytis cinerea* reached approximately 65, 99.9 and 99.9% at Ag nanoparticle concentrations of 10 ppm, 50 ppm, and 100 ppm, respectively [21].

Table I. Antifungal efficiency of Ag nano/SiO_2 against *Aspergillus niger* van Tieghem with various concentrations of Ag nano

Concentration of Ag nano in Ag nano/SiO_2	**Number of fungal cells (CFU/ml)**	**Inhibitory percentage (η, %)**
0 ppm (Control)	1.8×10^6	0
30 ppm	6.4×10^5	64
50 ppm	5.2×10^5	71
70 ppm	3.4×10^5	81
100 ppm	3.1×10^5	82
150 ppm	7.1×10^4	96

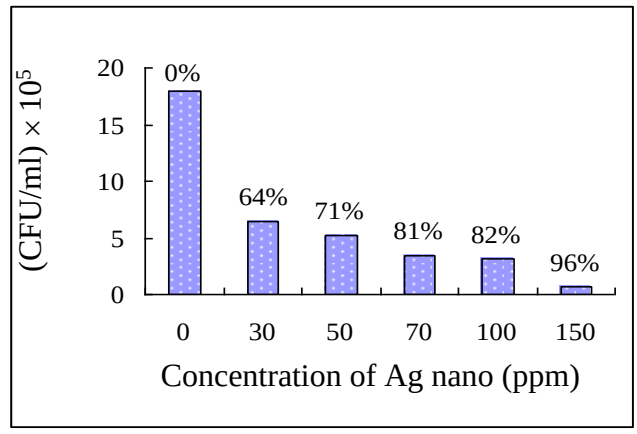

Fig. 4. Antifungal efficiency of Ag nano/SiO_2 against *Aspergillus niger* van Tieghem with various concentrations of Ag nano

III. CONCLUSIONS

Silver nanoparticles entrapped onto SiO_2 **(**Ag nano/SiO_2) were successfully synthesized by gamma irradiation. These nanoparticles exhibited a size range of 5 to 20 nm when they were prepared with the suspension containing 5 mM Ag^+. The average crystal size of the Ag nanoparticles was about 23 nm, and they displayed a face centered cubic structure as indicated in their XRD patterns. The antifungal efficiency of Ag nano/SiO_2 was remarkable, with inhibitory percentage of 64, 71, 81, 82 and 96% observed at Ag nanoparticle concentrations of 30 ppm, 50 ppm, 70 ppm, 100 ppm, and 150 ppm, respectively. These results suggested that Ag nano/SiO_2 can be used as a potential antifungal agent in various applications, especially in toothpaste, paint, cosmetics,.. .

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